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1,2-DIOXETANES: FORMATION, MECHANISM OF THERMOLYSIS AND EFFICIENCY--ETC(U)
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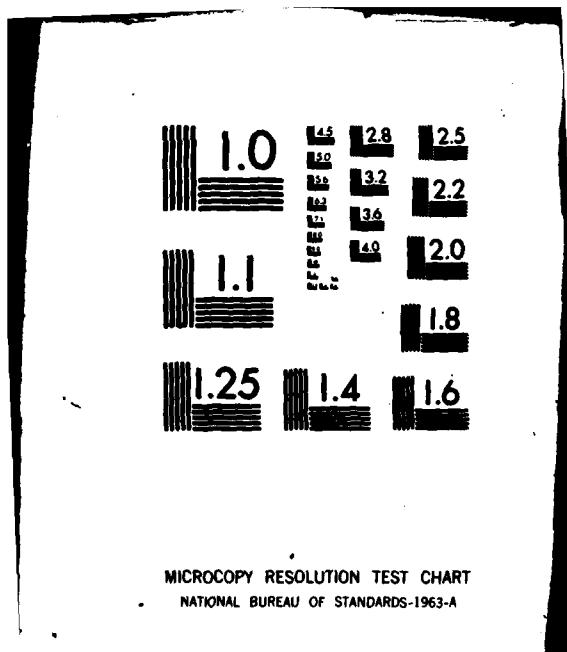
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| 19. ABSTRACT (Continue on reverse side if necessary and identify by block number) The production of excited molecules from a chemical reaction is limited to a small, but growing group of molecules. Applications of these reactions to produce light (chemiluminescence, CL) has been used for marking and viewing, and for analytical purposes. 1,2-Dioxetanes have been one of the most important types of compounds in studies of CL processes. It is in this area that our research has been directed. | | |

20. Abstract (continued)

One phase of our research has been directed to a study of the mechanism of dioxetane thermolysis. Since the CL process will be intimately related to the mechanism of thermolysis, we have been interested to define the parameters that control the mechanism. Currently three mechanisms are considered: (1) stepwise biradical; (2) concerted; and (3) electron transfer (CIEEL). The latter mechanism is apparently applicable to dioxetanes which possess a good reducing substituent (e.g., amino). In simply substituted dioxetanes (without good reducing groups) our results support a stepwise mechanism. We have searched for dioxetanes that would exhibit a concerted decomposition. One such dioxetane has been prepared that has the potential to undergo a concerted decomposition. Studies are in progress to determine if a concerted process occurs.

A key intermediate in the thermolysis of dioxetanes by the stepwise process is the 1,4-dioxy biradical. Attempts have been made to estimate the lifetime of this biradical by competitive β -scission and by trapping with hydrogen atom donors. We have been unable to detect products that are indicative of a biradical in these experiments. The lifetime of the biradical can be bracketed between 10^{-12} to 10^{-13} (vibrational lifetime) sec from these experiments. Substituent effect data support a biradical intermediate, but it appears that the biradical is a fleeting intermediate. *beta*

The efficiency of producing an excited state carbonyl product from a dioxetane varies widely. We have been interested in establishing the structural features of dioxetanes that determine efficiency. We have found that both electronic and steric effects influence the efficiency. To study solely electronic effects, we have prepared a series of para-and meta-substituted 3-aryl-3-methyl-1,2-dioxetanes where steric effects are held constant. To our surprise both electron releasing and electron withdrawing groups decrease the triplet efficiency. A decrease in the triplet energy of the pro-acetophenone portion of the dioxetane ($E_T(\text{ArCOCH}_3)$) causes a decrease in the triplet efficiency (α_T). A crude linear relationship is given by $E_T(\text{ArCOCH}_3)$ vs $\log \alpha_T$. Currently, our best explanation for this observation involves the initial formation of an exciplex. Several other substituted dioxetane systems are now under investigation to test this proposal.

In the course of this study we have employed a new low energy acceptor for measuring triplet efficiencies (6,12-dibromotetracene (DBT)). We have observed triplet, singlet energy transfer with DBT and acetophenones, but not with DBT and alkanones. This observation has consequences to the mechanism of triplet, singlet energy transfer and has the practical value of determining specific efficiencies of aryl ketones in the presence of alkanones.

Both from a practical and theoretical view, it was important to understand how the excitation energy was distributed between dissimilar carbonyls produced from a dioxetane. A Boltzmann distribution based on triplet energies of the carbonyl products served as a good predictive tool for several simply substituted dioxetanes. A further analysis of this model with 3,3-dibenzyl-1,2-dioxetane reveals that the efficiency of the carbonyl product with the higher triplet energy may be underestimated by this procedure. This effect may be greatest when the difference between triplet energies of the carbonyl products is greatest.

We have initiated some work directed to observing excited state production from the thermolysis of amino-substituted dioxetanes. α -Amino peroxides, incorporated into flavin systems, have been invoked as intermediates in bacterial luminescence. We have pursued the possibility of CL with two energy sufficient simple α -amino peroxides. In neither case was there evidence for excited state production in the thermolysis. Although sufficient energy is required in the reaction to

20. Abstract (continued)

produce excited states, it is clear that the mechanism of thermolysis is also important. Further studies in this area are continuing.

We are in the process of increasing our data collection and processing capabilities with a microcomputer. Several programs have been written in Basic for this purpose. We are in the process of interfacing the computer to our light measuring apparatus, so that data can be rapidly collected and processed. The computer is also interfaced to a digital plot, so that our results can be plotted as well.

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1,2-Dioxetanes, Formation, Mechanism of Thermolysis and
Efficiency of Excited State Carbonyl Production

Final Report

William H. Richardson

14 October 1980

U. S. Army Research Office

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San Diego State University

TABLE OF CONTENTS

| | |
|---|----|
| Report of Documentation Page. | i |
| Abstract. | i |
| Report Text | |
| Introduction | 1 |
| Mechanistic Studies of Dioxetane Thermolyses | 1 |
| Estimates of 1,4-Dioxy Biradical Lifetimes | 3 |
| Efficiency of Excited State Carbonyl Production from Dioxetanes. | 5 |
| Excited State Energy Distribution. | 7 |
| Excited States from Amino-Substituted Peroxide Thermolysis | 9 |
| Microcomputer Applications | 10 |
| Bibliography | 11 |
| Appendices (Tables). | 13 |
| Publications | 16 |
| Personnel. | 17 |

1,2-Dioxetanes, Formation, Mechanism of Thermolysis and Efficiency of Excited State Carbonyl Production

Final Report

Introduction

The production of excited state molecules in a chemical reaction has received increased attention in the last decade.¹ There has also been a wide range of disciplines interested in these reactions. For example, research in biology, biochemistry, organic chemistry, and physical chemistry have been directed to bioluminescent (BL) and chemiluminescent (CL) reactions.²

In addition to the fundamental interest in BL and CL reactions, several applications have been made. Most of the applications can be divided into two categories: (1) the production of light for marking or viewing purposes;³ and (2) the use of CL reactions for analytical purposes.^{4a} Recently, numerous CL bioassays have been developed.^{4bcd} Many of these methods are attractive alternatives to radioassays.

Yet, with this interest and application of BL and CL reactions, the fundamental aspects of these reactions are only partially understood. Our research in this area has been with 1,2-dioxetanes, which are relatively simple molecules and thus appear to have a greater potential for understanding the fundamental CL processes. Even so, there is still a considerable lack of understanding of CL processes with dioxetanes. Currently there are three mechanisms that are considered for the thermolysis of dioxetanes: (1) stepwise biradical;⁵ (2) concerted;⁶ and (3) electron transfer (CIEEL).⁷ The operation of these mechanisms is structurally dependent and some broad guidelines are now available as to when these mechanisms are applicable. However, there is not universal agreement on these guidelines and the details of structure *vs* mechanism need further refinement. Even more obscure is the mechanism by which electronically excited states are produced from dioxetanes. Although general mechanisms are given for the chemi-excitation process, there is not a clear understanding of the process. Considerable more experimental work is required before a meaningful understanding is obtained. For example, although many dioxetanes have been studied, the relationship between substituent effects and efficiency of excited carbonyl production is poorly understood. This analysis of the understanding of CL reactions may seem pessimistic, yet the possibilities for significant contribution in this area are great.

Our research with dioxetanes has been directed to defining the mechanism of dioxetane thermolysis, including attempts to provide evidence for biradical intermediates; the effect of dioxetane structure on efficiency of excited state production; excited state energy distribution between dissimilar carbonyls produced from a dioxetane; and CL from amino-substituted peroxides.

Mechanistic Studies of Dioxetane Thermolysis

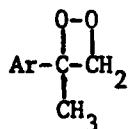
In order to understand the chemi-excitation process, one must understand the mechanism of dioxetane thermolysis. As indicated above, currently there are three mechanisms under consideration:

(1) stepwise biradical;⁵ (2) concerted;⁶ and (3) electron transfer (CIEEL).⁷ The CIEEL process is characterized by dioxetanes substituted with aryl groups possessing groups with low oxidation potentials. With dioxetanes which do not possess these substituents ("simply substituted dioxetanes"), the results from our laboratory and others favor the stepwise biradical mechanism over the concerted process.⁵ We have been interested in the design of dioxetanes that may lead to a documented concerted reaction. Thus, one may be able to find a progression in mechanism from stepwise to concerted to CIEEL. In the search for such a progression to a concerted process, we have studied the thermolysis of triphenyl-1,2-dioxetane (λ)^{5g} and 3,3-bis-p-anisyl-1,2-dioxetane (λ).^{5f} In



both instances, the results are more conveniently explained in terms of a stepwise rather than a concerted process. The details of these studies have been published^{5g,f} during the period of this grant.

More recently we have studied the thermolysis of the series of dioxetanes (λ) shown below.



- λ_a , Ar = C_6H_5
- λ_b , Ar = $\text{p-CH}_3\text{OC}_6\text{H}_4$
- λ_c , Ar = $\text{p-CH}_3\text{C}_6\text{H}_4$
- λ_d , Ar = $\text{p-BrC}_6\text{H}_4$
- λ_e , Ar = $\text{m-BrC}_6\text{H}_4$
- λ_f , Ar = $\text{m-CF}_3\text{C}_6\text{H}_4$
- λ_g , Ar = $\text{p-NO}_2\text{C}_6\text{H}_4$

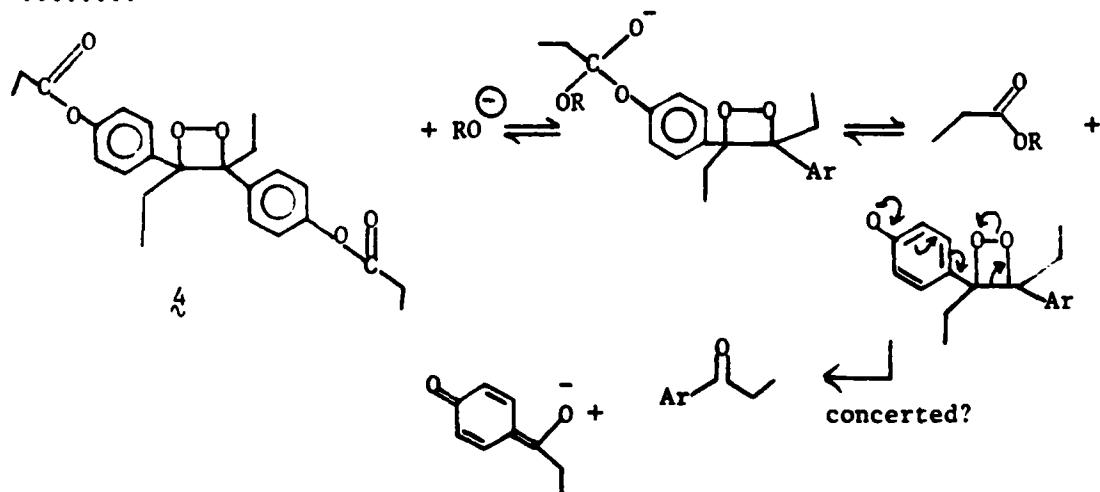
Here steric effects are held constant, so a more reliable mechanistic probe can be made with variations in electronic effects only. Excluding the p-methoxy derivative (λ_b) from a Hammett plot, the data are well correlated with $\rho = -0.219 \pm 0.037$ ($r = 0.948$, standard deviation estimate in $\log k/k_0 = \pm 0.0275$). Relative to this plot, λ_b is 1.7-fold faster than expected. If Brown-Hammett plot is used all of the series λ dioxetanes (including λ_b) are well correlated with $\rho = -0.286 \pm 0.044$ ($r = 0.946$, standard deviation estimate in $\log k/k_0 = \pm 0.057$). The small negative ρ -values are consistent with an initial homolysis of the peroxide bonding in λ via a stepwise process. ρ -Values of this magnitude are observed in the homolysis of the peroxide bond in benzoyl peroxides ($\rho = -0.38$). A considerably more negative ρ -value is expected if a concerted process was operative, where a partially positively charged carbonyl carbon atom is entering into conjugation with the aryl group in the activated complex. The origin of the attenuated rate acceleration by p-methoxy (λ_b) is uncertain, although it is

possible that we may be realizing a small contribution to a concerted process here.

It was desired to extend series 3 to dioxetanes which contained p -(CH₃)₂N- and p -CH₃S-substituents, where electron transfer mechanisms might be operative. A considerable effort was made to prepare the p -(CH₃)₂N-derivative without success. We could obtain a crude preparation of the bromohydroperoxide precursor (p -(CH₃)₂C₆H₄C(CH₃)(OOH)CH₂Br), but we were unable to obtain the dioxetane upon treatment of this hydroperoxide with base. Under the conditions used for bromohydroperoxide preparation, thioanisole (CH₃SC₆H₅) undergoes reaction with hydrogen peroxide to give the sulfoxide. Thus, we did not attempt the synthesis of 3 with a p -CH₃S-substituent.

We have been able to synthesize dioxetane 4, which has the potential for a concerted reaction. The proposed scheme by which 4 may undergo decomposition in a concerted manner is shown below. The basic decomposition of 4 is

Scheme I



currently under study.

In summary, simply substituted dioxetanes appear to undergo a stepwise decomposition with initial homolysis of the peroxide bond to give a 1,4-dioxy biradical intermediate. Other laboratories have shown that with low oxidation potential substituents, an electron transfer process (CIEEL) can occur.⁷ With appropriate substitution dioxetanes may be induced to undergo either concerted or CIEEL processes; however, we have observed no evidence of a concerted process as yet.

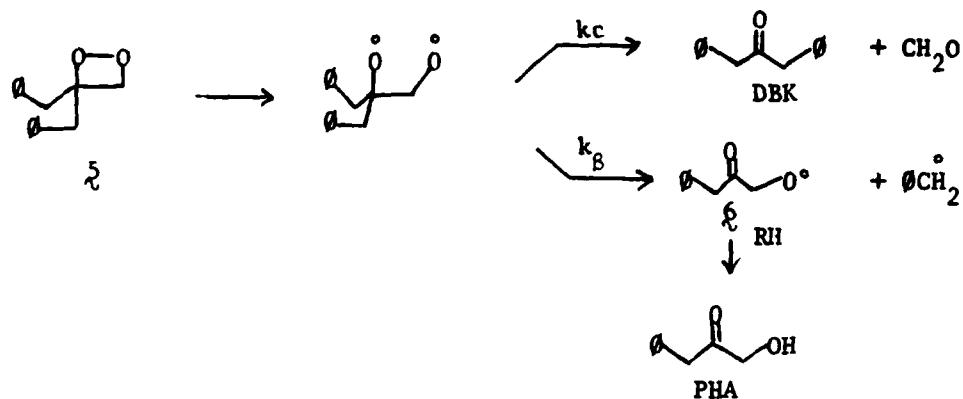
Estimates of 1,4-Dioxy Biradical Lifetimes

Early estimates by us indicated that 1,4-dioxy biradical lifetimes might be as long as a nanosecond (ns)^{5b}. With lifetimes as long as a ns, it would be possible to provide evidence for the biradical in the thermolysis of dioxetanes

by competitive processes or by trapping reactions.

A competitive β -scission process has been used to estimate the biradical lifetime in the thermolysis of 3,3-dibenzyl-1,2-dioxetane (ζ) as shown in Scheme II. The relative rate k_c/k_B can be determined from eq 1. With an

Scheme II

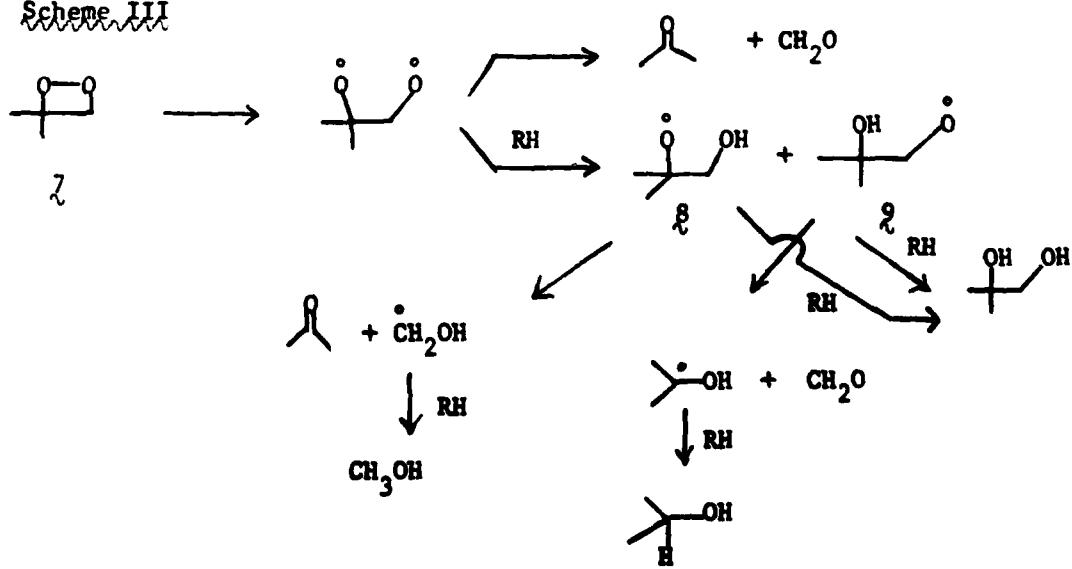


$$k_c/k_B = [\% \text{ yield DBK}] / [\% \text{ yield PHA}] \quad (1)$$

estimate for $k_B (1.1 \times 10^8 \text{ sec}^{-1} \text{ at } 45^\circ)$, one can then calculate k_c and thus the lifetime of the biradical ($\tau = 1/k_c$). We have shown that the alkoxy radical $(\text{CH}_3)_2\text{CHCO}(\text{O}^\bullet)(\text{CH}_3)_2$ can be efficiently trapped with a good hydrogen atom donor such as cyclohexene or cyclohexane. Decomposition of ζ was carried out in cyclohexene, cyclohexane, and benzene (for reference) and an HPLC analysis was made for DBK and PHA. Within our detectability limits, no PHA was observed. With these detectability limits, the maximum lifetime of the biradical is 10^{-12} sec , (cyclohexene). Since the minimum lifetime of the biradical (vibrational lifetime) is about 10^{-13} sec , these results bracket the biradical lifetime between 10^{-12} to 10^{-13} sec .

Trapping experiments of the biradical produced from 3,3-dimethyl-1,2-dioxetane (ζ) with cyclohexene have been attempted (Scheme III). Presently, we have been

Scheme III



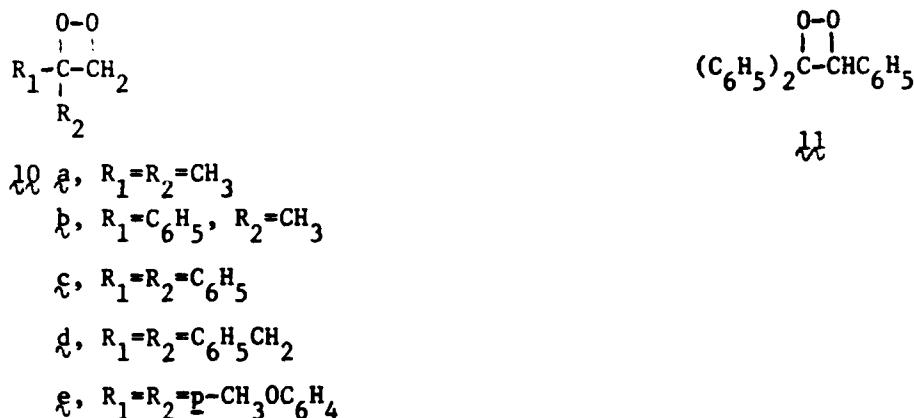
unable to detect the glycol by glc analysis. With our detectability limits, this gives a maximum lifetime for the biradical of about a ns. The possibility exists that alkoxy radicals δ and η may undergo rapid β -scission, so that glycol is not observed. Instead, isopropyl alcohol and methanol would be formed. We are presently checking for these products.

In summary, the kinetic data support a stepwise biradical mechanism, but it appears that the biradical intermediate is very short lived.

Efficiency of Excited State Carbonyl Production from Dioxetanes

We have been interested in establishing the structural features of dioxetanes that determine the efficiency of excited state carbonyl production. The thermochemistry allows the formation of one excited state carbonyl molecule/dioxetane molecule (100% efficiency). Observed triplet efficiencies range from about tenths of a percent to 60% in simply substituted dioxetanes.⁹ With an understanding of how the dioxetane structure effects efficiency, one could design dioxetanes for maximum efficiency.

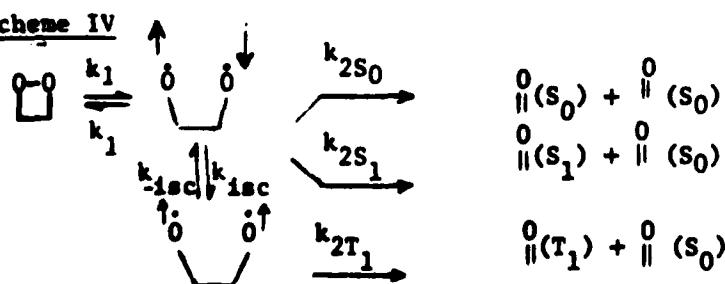
We have published our results on the efficiencies of dioxetanes $10a-e$ and 11 during the period of this grant.⁹ This publication may be consulted for the details of



this work. In general, it was found that increased phenyl substitution or substitution by strongly electron releasing groups decreased the triplet efficiency.

Since it was apparent from the above results that both electronic and steric effects influenced the efficiency, we then studied a series of dioxetanes (3) where steric effects were held constant and only electronic effects were varied. To our surprise all substituents decreased the triplet efficiency as seen from Table 1. Based on the simple stepwise biradical process (Scheme IV), we anticipated that electron withdrawing groups would increase the triplet efficiency, while electron releasing groups would decrease the triplet efficiency. The rationalization for this conclusion is as follows. Electron withdrawing groups are

Scheme IV

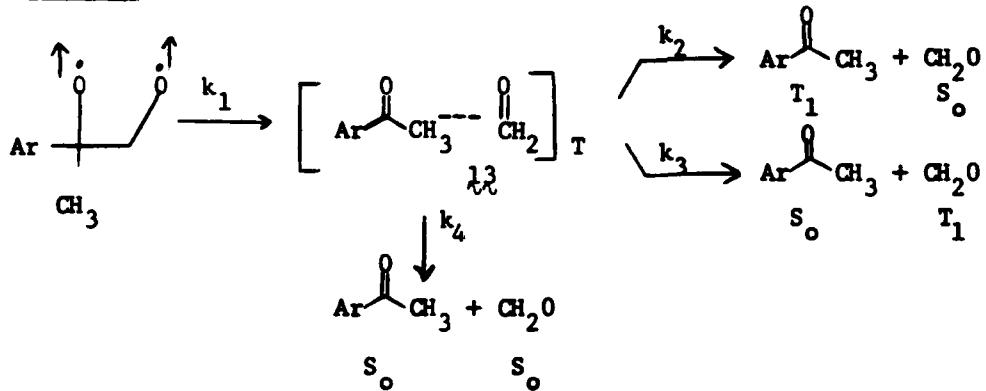


are expected to decrease k_{2S_0} , while they should have little effect of Kisc (= kis/k-isc). This in turn could drive the decomposition of the biradical to triplet products. The converse of this argument would predict lower triplet yields with electron releasing substituents. It is clear from Table I that these expectations were not met.

Another surprising feature of substituent effects on efficiency was noted. In other studies we observed that the triplet excited state energy distribution between dissimilar carbonyl products, formed from simply substituted dioxetanes, was correlated by a Boltzmann distribution of their triplet energies.¹⁰ This distribution was established for 3a (see later). With such a Boltzmann distribution, the specific triplet efficiencies for the acetophenones and formaldehyde can be calculated and are shown in Table II. It can be seen that the specific triplet efficiency for the acetophenones (% a_T (ArCOCH_3)) is constant with the variation in substitution, while the differences in total efficiencies are manifested in formaldehyde.

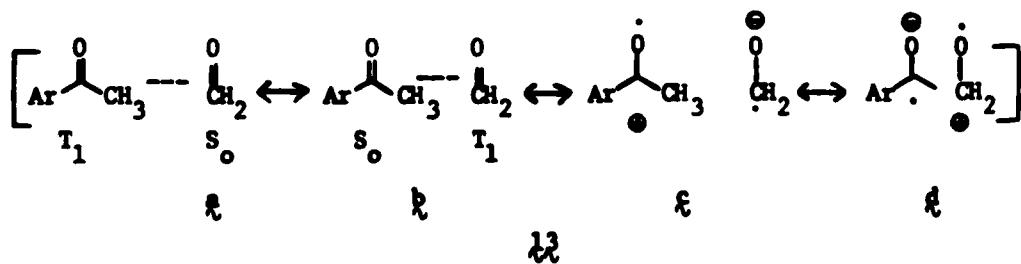
This application of the Boltzmann distribution leads one to the surprising conclusion that substituent variation in the acetophenone portion causes efficiency changes in solely the formaldehyde portion. This untenable conclusion has forced us to propose that an exciplex is formed initially. With the exciplex proposal, one can explain the communication of substituent effect variations in the acetophenone portion to the formaldehyde fragment. The exciplex scheme, originating from the triplet biradical is shown below:

Scheme V



Deactivation of the triplet exciplex to ground state carbonyls in Scheme V has an analogy in the photodimerization of cyclohexanone and cyclopentanone via a triplet excimer.¹¹

The exciplex in Scheme V can be written in terms of canonical structures as shown below. Lowering



the triplet energy of ArCOCH_3 ($E_T(\text{ArCOCH}_3)$) will lower the energy of exciplex λ_3 via the contribution of λ_3 a. A crude linear plot of $E_T(\text{ArCOCH}_2)$ vs $\log \alpha_T$ (total) is observed, where α_T (total) was decreased with lower $E_T(\text{ArCOCH}_3)$ values. The exciplex proposal suggests that the substituent effects in Ar should be dependent on the other carbonyl portion (e.g., CH_2O in Scheme V). To test this proposal we are currently investigating the replacement of the CH_2O portion of λ_3 with carbonyl moieties of significantly higher and lower; and equal triplet energy compared to ArCOCH_3 . In λ_3 , $E_T(\text{ArCOCH}_3)$ ranges to a few kcal above $E_T(\text{CH}_2\text{O})$ to a few kcal below $E_T(\text{CH}_2\text{O})$. Our current proposal is that decreasing the energy of the exciplex will increase its lifetime and thus increase k_4 relative to $(k_2 + k_3)$. This will result in lower triplet efficiencies with lower energies of the exciplex.

Two additional features can be noted with regard to efficiencies in the series λ dioxetanes. As mentioned above a crude linear plot of $E_T(\text{ArCOCH}_3)$ vs $\log \alpha_T$ (total) is observed. Both of the bromo-substituted derivatives ($\lambda_3\text{d}$ and $\lambda_3\text{e}$) are correlated by this relationship, so heavy atom effects are not involved in determining efficiencies. Next, the relative placement of n,π^* and π,π^* energies varies in the pro-acetophenone portion of these dioxetanes.¹² Since no deviations are noted with this effect compared to the $E_T(\text{ArCOCH}_3)$ vs $\log \alpha_T$ (total) plot, one must conclude that n,π^* vs π,π^* energies in the pro-acetophenone portion of the dioxetane do not influence efficiency.

During the course of this investigation we were concerned about possible inefficient energy transfer from triplet acetophenones to 9,10-dibromoanthracene (DBA). This inefficiency of energy transfer could conceivably explain the low triplet efficiencies. To investigate this point we have studied the energy transfer to 6,12-dibromotetracene (DBT), where the excited singlet energy is estimated to be 56 kcal/mol and well below any of the acetophenones. These studies opened another interesting aspect of our research. Namely that whereas the acetophenones undergo triplet, singlet energy transfer with DBT, the alkanones do not. Thus, triplet, singlet energy transfer between triplet acetone produced from tetramethyl-1,2-dioxetane is not observed. In addition, the triplet, singlet energy transfer from the series λ dioxetanes is that expected, on the basis of a Boltzmann distribution, as resulting from only the acetophenone portion. The results with DBT and the series λ dioxetanes are given in Table III. This suggests that energy transfer with DBT operates by a direct triplet, singlet process, which is determined by the overlap of the emission of the donors (acetophenones) and the absorption of the acceptor (DBT). This contrasts with a recent report that this type of energy transfer occurs by a collisional process involving initial T_1 (donor), T_2 (acceptor) energy transfer.¹³

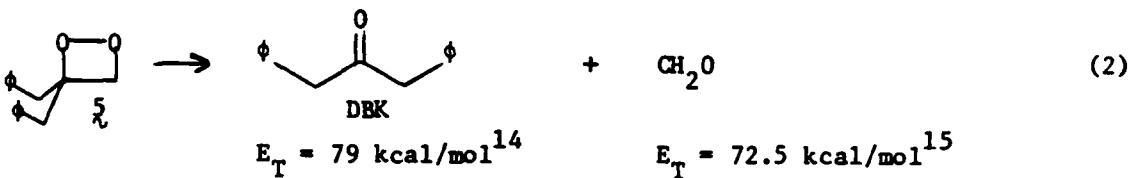
Excited State Energy Distribution

Unsymmetrically substituted dioxetanes will undergo thermolysis, where the excitation energy is distributed in some manner between the dissimilar carbonyl products. It would be interesting to be able to predict how the excitation energy is distributed and to have some theoretical insight into the mode of distribution. We have carried out such a study and the results were published during the period of this grant.¹⁰

Simply substituted dioxetanes were studied and two models for excited state energy distribution were considered: (1) a Boltzmann model, based on the triplet energies (E_T) of the carbonyl products; and (2) a vibrational model, based on the number of vibrational modes in each pro-carbonyl portion of the dioxetane. Of these two models, the data were well correlated by the Boltzmann model, but not by the vibrational model.

The generality of the Boltzmann model still needs further investigation. Although the Boltzmann model gives a good prediction of the energy distribution in the simply substituted dioxetanes that we have studied, the absolute fit to this model is uncertain. This is due to several factors. For example, the energy distribution is related exponentially to triplet energies, so that small changes in E_T (or error) can cause large differences in the distribution. Also, this is a ground state product model and how well it reflects the activated complex is uncertain.

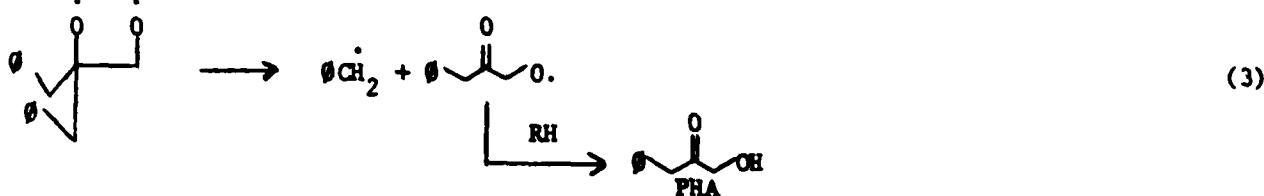
One system that has interested us with regard to the Boltzmann distribution is 3,3-diphenyl-1,2-dioxetane (ξ). The overall triplet



efficiency of ξ is 22%⁹ and with triplet energies given in eq. 2, the Boltzmann model predicts about $8 \times 10^{-4}\%$ triplet DBK at 45°. However, our earlier quenching studies with 9,10 diphenylanthracene (DPA) indicated a specific triplet efficiency for DBK of 2%.¹⁶ In these studies, ξ was decomposed with varying concentrations of DPA and the yield of bibenzyl was measured. From a Stern-Volmer plot, the specific efficiency of DBK was obtained. The lifetime of triplet DBK, obtained from the Stern-Volmer plot, was about 10-fold longer than reported.¹⁴ Considering the deviation in the Boltzmann prediction vs the observed efficiency and the difference in lifetimes, we were concerned that we may not have been monitoring the DBK triplet. That is, the possibility existed that bibenzyl resulted from a reaction other than the Type-I reaction of triplet DBK.

To pursue this problem, we studied the decomposition of *t*-butyl perphenylacetate ($C_6H_3CO_3C(CH_3)_3$) in the presence of varying concentrations of DPA in benzene. The perester is a source of benzyl radicals, and we could then determine the trapping of these radicals by DPA by monitoring yields of bibenzyl. With these results, we were able to correct the yields of bibenzyl produced from coupling of benzyl radicals in the thermolysis of ξ with DPA in benzene. The Stern-Volmer plot with the corrected yields of bibenzyl gave a lifetime from the slope which was in agreement with the reported lifetime of DBK triplet.¹⁴ This added support to our initial proposal that triplet DBK was produced from ξ .

Next, in our biradical trapping studies we found no evidence for phenyl hydroxy acetone (DHA), which would be the companion product of benzyl radicals resulting from the biradical (eq. 3).



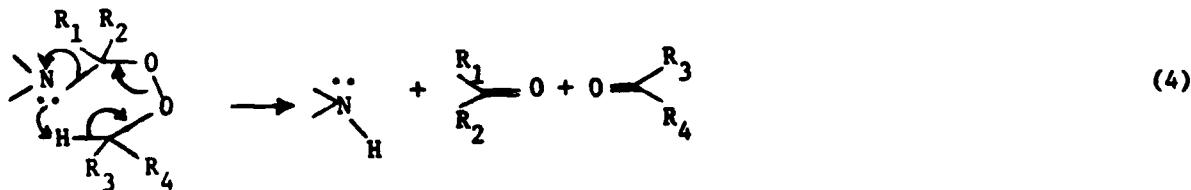
Since eq. 3 would provide the most likely alternative route to benzyl radicals vs triplet DBK, the lack of PHA provides added support to triplet DBK as the source of benzyl radicals, and thus bibenzyl, from dioxetane 5.

From this analysis of the triplet energy distribution in the carbonyl products formed from 5, it is seen that in this case the Boltzmann model is only approximate. The apparent triplet efficiencies from 5 are 2% DBK and 20% formaldehyde, rather than essentially no DBK triplets and 22% formaldehyde triplets as expected from the Boltzmann model. We feel that the most likely explanation for this discrepancy is in the use of differences in product energies to represent differences in the activation energies. That is, in the reaction of the triplet biradical to give either $\text{DB}(T_1) + \text{CH}_2\text{O}$ or $\text{DBK} + \text{CH}_2\text{O}(T_1)$, the full difference in energy between $\text{DBK}(T_1)$ and $\text{CH}_2\text{O}(T_1)$ ($=6.5 \text{ kcal} = 79-72.5$) is not reflected in the activated complex. Instead, only a portion of this energy difference between the products is reflected in the activated complex ($1.5 \text{ kcal/mol} = RT \ln 20\%/2\%$, assuming constant A-values). This is consistent with expectations from a highly exothermic reaction, which in turn is consistent with our attempts to trap the biradical. Furthermore, an exciplex may precede the dissociated carbonyl products (see above), which may effect the application of the Boltzmann product model.

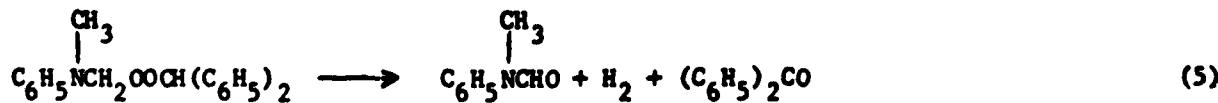
In summary, the Boltzmann model gives good predictions of triplet excitation energy distribution for some dioxetanes. In other cases, possibly when the triplet carbonyl energies differ greatly, the model underestimates the triplet efficiency of the higher energy triplet carbonyl.

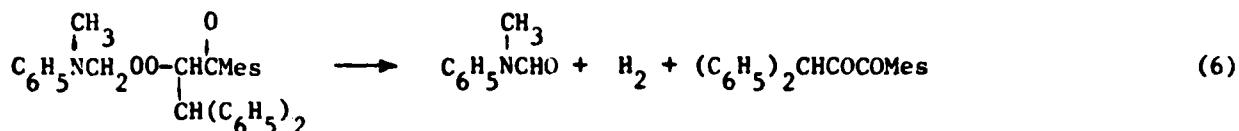
Excited States from Amino-Substituted Peroxide Thermolysis

A possible mechanism for bacterial luminescence in the flavin system involves fragmentation of an α -amino peroxide (eq. 4).¹⁷ Thermochemical calculations



indicate that this reaction is energy sufficient to produce a carbonyl species in an excited state. It was desired to test this reaction with some simple α -amino peroxides, rather than the flavin system. Two α -amino peroxides were prepared (14 and 15), but the thermolysis paths did not follow eq. 4. Instead eqs. 5 and 6 were followed, where both of these paths were also energy sufficient to generate an excited state carbonyl molecule.¹⁸ In neither reaction 5 or 6, was there evidence for excited state carbonyl





15, Mes = mesityl

production. Thus, although a reaction must be energy sufficient to produce excited state products, it does not guarantee excited state production. In other words, a "correct" mechanism is required in addition to energy sufficiency for excited state production.

Since the possibility exists for the electron transfer CL (CIEEL) in molecules that possess an oxidizing group and a reducing group,⁷ we are currently surveying other amino peroxides for excited state production.

Microcomputer Applications

We are in the process of increasing our data collection and processing capabilities with the use of a 6809 Motorola based microcomputer. The relative low cost of these computers makes such applications attractive.

Several programs have been written in Basic for data processing that will be useful to our research. Some of the programs are: first-order kinetics calculations, activation parameter calculations, efficiency calculations, and linear free energy relationships. Some software has been written for a Houston digital plotter, which is interfaced to the computer. These plotting routines can then be incorporated into the various programs.

We are in the process of interfacing the computer to our light measuring apparatus. With this interface we can collect and store the data; and then process it to give first-order rate coefficients and apparent quantum yields. We are also planning to interface our monochromator to the computer so that emission spectra from dioxetanes can be obtained. This should aid us in identifying the excited state species produced from dioxetanes. Finally, we are also in the process of interfacing via a Modem between our microcomputer and a campus VAX-computer. This will allow larger calculations and Fortran use via our microcomputer.

Bibliography

- (1) See P.D. Bartlett and M.E. Landis, Singlet Oxygen, H.H. Wasserman and R.W. Murray, ed., Academic Press, New York, N.Y., 1979, p. 243 and references therein.
- (2) See M.J. Cormier, D.M. Hercules, and J. Lee, ed., Chemiluminescence and Bioluminescence, Plenum Press, New York, N.Y., 1973.
- (3) M.M. Rauhut and G.W. Kennerly, Chem. Abstrs., 74, P265896 (1971).
- (4) (a) See T.S. Krull and M.H. Wolf, Amer. Lab., 11, 84 (1979); (b) Dupont (ATP); (c) Packard Instrument Co.; (d) Analytical Luminescence Laboratory, Inc.; (e) SAI Technology Co.
- (5) (a) H.E. O'Neal and W.H. Richardson, J. Amer. Chem. Soc., 92, 6553 (1970); (b) W.H. Richardson, M.B. Yelvington, and H.E. O'Neal, ibid., 94, 1619 (1972); (c) W.H. Richardson and H.E. O'Neal, ibid., 94, 8665 (1972); (d) W.H. Richardson, F.C. Montgomery, M.B. Yelvington, and H.E. O'Neal, ibid., 96, 7525 (1974); (e) W.H. Richardson, F.C. Montgomery, P. Slusser, and M.B. Yelvington, ibid., 97, 2819 (1975); (f) W.H. Richardson, J.H. Anderegg, M.E. Price, and R. Crawford, J. Org. Chem., 43, 4045 (1978); (g) W.H. Richardson, J.H. Anderegg, M.E. Price, W.A. Tappen, and H.E. O'Neal, ibid., 43 2236 (1978); (h) J.-Y. Koo and G.B. Schuster, ibid., 99, 5403 (1977).
- (6) N.J. Turro, P. Lechtken, N.E. Shore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, Acc. Chem. Res., I, 97 (1974).
- (7) (a) J.-Y. Koo and G.B. Schuster, J. Amer. Chem. Soc., 100, 4496 (1978); (b) S.P. Schmidt and G.B. Schuster, ibid., 100, 1966 (1978); (c) J.P. Smith and G.B. Schuster, ibid., 100, 2564 (1978); (d) J.-Y. Koo and G.B. Schuster, ibid., 99, 6107 (1977); (e) K.A. Zaklika, A.L. Thayer, and A.P. Schaap, ibid., 100, 4916 (1978); (f) F. McCapra, I. Behesti, A. Beerford, R.A. Hann, and K.A. Zaklika, J. Chem. Soc., Chem. Commun., 944 (1977); (g) F. McCapra, ibid., 946 (1977).
- (8) (a) A.T. Bloomquist and A.J. Buselli, J. Amer. Chem. Soc., 73, 3883 (1951); (b) C.G. Swain, W. Stockmayer, and T. Clarke, ibid., 72, 5426 (1950); (c) W.H. Richardson and H.E. O'Neal, Comprehensive Chemical Kinetics, Vol. 5, C.H. Bamford and C.F.H. Tipper, ed., Elsevier, New York, N.Y., 1972, p. 381.
- (9) See W.H. Richardson, J.H. Burns, M.E. Price, R. Crawford, M. Foster, P. Slusser, and J.H. Anderegg, J. Amer. Chem. Soc., 100, 7596 (1978) and references therein.
- (10) W.H. Richardson, M.B. Lovett, M.E. Price, and J.H. Anderegg, ibid., 101, 4683 (1979).
- (11) (a) P. DeMayo, Acc. Chem. Res., 4, 41 (1971); (b) P.J. Wagner and D.J. Buchak, J. Amer. Chem. Soc., 91, 5090 (1969).
- (12) Cf., P.J. Wagner, A.E. Kemppainen, and H.N. Schott, ibid., 95, 5604 (1973).
- (13) W. Adam, G. Cilento, and K. Zinner, Photochem. Photobiol., 32, 87 (1980).
- (14) P.S. Engel, ibid., 92, 6074 (1970).
- (15) J.C.D. Brand and D.G. Williamson, Advan. Phys. Org. Chem., 1, 365 (1963).

- (16) W.H. Richardson, F.C. Montgomery, and M.B. Yelvington, J. Amer. Chem. Soc., 94, 9277 (1972).
- (17) C. Kemal and T.C. Bruice, J. Amer. Chem. Soc., 99, 7064 (1977).
- (18) W.H. Richardson, J. Org. Chem., 45, 303 (1980).

Table 1. Triplet and Singlet Efficiencies of 3-Aryl-3-Methyl-1,2-Dioxetanes
in Benzene at 45°

| Ar | % α_{T_1} (Total) ^a | % α_{S_1} (Total) ^b |
|---|---------------------------------------|---------------------------------------|
| C ₆ H ₅ (3a) | 14 | 0.095 |
| p-CH ₃ OC ₆ H ₄ (3b) | 2.1 | .043 |
| p-CH ₃ C ₆ H ₄ (3c) | 4.5 | .053 |
| p-BrC ₆ H ₄ (3d) | 1.8 | .12 |
| m-BrC ₆ H ₄ (3e) | 2.5 | .16 |
| m-CF ₃ C ₆ H ₄ (3f) | 3.9 | .12 |
| p-NO ₂ C ₆ H ₄ (3g) | 0.99 | .058 |

^aDetermined by the 9,10-dibromoanthracene (DBA) method, where tetramethyl-1,2-dioxetane α_{T_1} = 36%. ^bDetermined by the 9,10-diphenylanthracene (DPA) method.

Table II. Specific Triplet Efficiencies for Acetophenones and Formaldehyde from 3-Aryl-3-Methyl-1,2-Dioxetanes as Calculated from a Boltzmann Distribution at 45° in Benzene.

| Aryl | % α_T (Total) | (kcal/mol) E_T (ArCOCH_3) | % α_T (ArCOCH_3) | % α_T (CH_2O) |
|--|-------------------------|---|---------------------------------------|---|
| C_6H_5 (3a) | 14 | 73.7 | 1.8 | 12.2 |
| p- $\text{CH}_3\text{OC}_6\text{H}_4$ (3b) | 2.1 | 71.8 | 1.6 | 0.53 |
| p- $\text{CH}_3\text{C}_6\text{H}_4$ (3c) | 4.5 | 72.9 | 1.6 | 2.9 |
| p- BrC_6H_4 (3d) | 1.8 | 71.1 | 1.6 | 0.17 |
| m- BrC_6H_4 (3e) | 2.5 | 72.5 | 1.3 | 1.3 |
| m- $\text{CF}_3\text{C}_6\text{H}_4$ (3f) | 3.9 | 72.6 | 1.8 | 2.1 |
| Av. 1.6±.1 | | | | |

Table III. Energy Transfer Between 3-Aryl-3-Methyl-1,2-Dioxetanes and DBT in Benzene at 45°

| Aryl | % α_T (Total) ^a | % α_T (DBT) ^b | % α_T (ArCOCH ₃) ^c |
|---|-----------------------------------|---------------------------------|--|
| C ₆ H ₅ (3a) | 14 | 2.4 | 1.8 |
| p-CH ₃ OC ₆ H ₄ (3b) | 2.1 | 1.6 | 1.6 |
| p-CH ₃ C ₆ H ₄ (3c) | 4.5 | 2.0 | 1.6 |
| p-BrC ₆ H ₄ (3d) | 1.8 | 1.6 | 1.6 |
| m-BrC ₆ H ₄ (3e) | 2.5 | 1.7 | 1.3 |
| m-CF ₃ C ₆ H ₄ (3f) | 3.9 | 1.9 | 1.8 |

^aObtained by the DBA method. ^bObtained by energy transfer to DBT and normalized to 3d. ^c Calculated by the Boltzmann E_T distribution with % α_T (Total).

PUBLICATIONS

1. W. H. Richardson, "Energy Sufficient α -Amino Peroxides as Potential Sources of Excited-State Carbonyls," *J. Org. Chem.*, 45, 303 (1980).
2. W. H. Richardson, M. B. Lovett, M. E. Price, and J. H. Anderegg, "Excited State Energy Distribution between Dissimilar Molecules Produced from 1,2-Dioxetanes," *J. Amer. Chem. Soc.*, 101, 4683 (1979).
3. W. H. Richardson, J. H. Burns, M. E. Price, R. Crawford, M. Foster, P. Slusser, and J. H. Anderegg, "The Effect of Aryl Substituents, Solvents, and Steric Effects on the Efficiency of Excited-State Carbonyl Production from 1,2-Dioxetanes," *J. Amer. Chem. Soc.*, 100, 7596 (1978).
4. W. H. Richardson, J. H. Anderegg, M. E. Price, and R. Crawford, "Kinetics of the Thermolysis of 3,3-(*p*-Anisyl)-1,2-dioxetane," *J. Org. Chem.*, 43, 4045 (1978).
5. W. H. Richardson, J. H. Anderegg, M. E. Price, W. A. Tappen, and H. E. O'Neal, "Kinetics and Mechanisms of the Thermal Decomposition of Triphenyl-1,2-dioxetane," *J. Org. Chem.*, 43, 2236 (1978).

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